

THE EFFECTS OF VELOCITY ON THE CATHODIC
PROTECTION OF ALUMINUM ALLOY
5086 IN SEA WATER

Richard Hardwicke Rice

THE UNIVERSITY OF MIAMI

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By

RICHARD HARDWICKE RICE, JR.

A THESIS

Submitted to the Faculty
of the University of Miami
in partial fulfillment of the requirement for
the degree of Master of Science

Coral Gables, Florida

August 1970

Thesis
R3757

T134541

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RICE, RICHARD HARDWICKE, JR. (M. S., Ocean Engineering)

The Effects of Velocity on the Cathodic Protection of Aluminum Alloy 5086 in Sea Water. (August 1970)

Abstract of a Master's Thesis at the University of Miami.
Thesis supervised by Professor Kenneth G. Compton.

The quantitative effects of sea water velocity on the cathodic protection of aluminum alloy 5086 are studied in this thesis. At velocities from 0 to 3 knots, two types of tests were conducted: 1) cathodic polarization curves, and 2) current density versus time. The results indicate that increasing the velocity of sea water past this alloy affects its polarization characteristics in two ways, the open circuit potential becomes more negative, and the current density required to maintain a given potential increases. Limited data indicate that a shift of -100 mV from the open circuit potential appears to be an adequate criterion for the cathodic protection of this alloy.

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Aluminum Alloy 5086 in Sea Water"

Richard Hardwicke Rice, Jr.

PREFACE

Despite the increasing use of magnesium-aluminum alloys in the sea, there is little information available on the cathodic protection of these alloys. It was proposed by Professor K. G. Compton that a study be made of the effects of velocity on the cathodic protection of magnesium-aluminum alloy 5086 in sea water.

This alloy was tested at velocities from 0 to 3 knots in a natural sea water test facility at the Rosenstiel School of Marine and Atmospheric Sciences. Cathodic polarization curves were obtained at several velocities, and the effect of velocity on the current density required for cathodic protection was studied.

I wish to express my deep appreciation to Professor K. G. Compton for proposing the subject investigation and for his wise counsel and continued inspiration. I would also like to thank Mr. C. A. Smith for his competent and timely suggestions.

Coral Gables, Florida
August, 1970

Richard Hardwicke Rice, Jr.

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INTRODUCTION

The purpose of this investigation was to determine a criterion for the cathodic protection of aluminum alloy 5086 in sea water, with particular emphasis on the effect of velocity. Although the effect of velocity on corrosion has been observed and discussed for many years, few investigations have been conducted with natural sea water. Additionally, little information is available on aluminum, or is qualitative rather than quantitative and, hence, is of marginal use to those interested in the design of cathodic protection systems for this alloy. Therefore, this investigation was undertaken to obtain quantitative data which would be useful in the design of such a system.

Background

In the words of Copson (1), "Generally corrosion increases with velocity, but [sometimes] the effect may be just the opposite." This statement reflects the heterogeneous nature of the information related to this subject which is available in the literature. In the complex field of corrosion testing there are many testing techniques, each with its own particular emphasis and method of reporting, and this complexity leads to difficulty both in interpretation and comparison of test results.

Several authors have reported on the effects of velocity on the corrosion of metals other than aluminum, and in various solutions, but in these reports they have also proposed general findings which may be applicable to aluminum. Romeo et al. (2) investigated steel pipes carrying synthetic tap water with a pH of 8.05 at velocities up to 4 ft/sec. It was found that the mechanical effects of the water flow on anodes and cathodes are of little importance because there is no flow of importance within the corrosion product layer, and thus, the transfer of chemicals such as oxygen is accomplished mainly by diffusion. However, very high velocities can modify or prevent the formation of such protective layers of corrosion products through mechanical effects. Additionally, they report that the presence of oxygen is in many cases the determining factor, and thus, the corrosion rate is often a function of the rate at which the oxygen diffuses through the corrosion product layer as well as the oxygen concentration of the electrolyte. They do, however, report that tests which do not closely simulate field conditions should be avoided as they often produce misleading results, and that velocity by itself is not a basis for comparing corrosion testing results obtained under hydraulically different conditions.

Copson (3) reports that a small amount of motion generally tends to make conditions more uniform, thus tending to make corrosion uniform and prevent local attack. Also, corrosion tests are more reproducible when there is some motion. However, motion may set up turbulence, and such turbulence may produce nonuniform conditions which may lead to pitting. It was also found that corrosion rates usually decrease with time, which is due in part

to a gradual thickening of protective films. Thus, if the films are thick enough, changes in velocity may be unnoticed at the metal surface. At high velocities there may be local breakdown of this film and thus, rapid pitting (4).

Among those testing aluminum, Wright et al. (5) used 2" x 2" x 0.064" coupons of 2S (1100) aluminum alloy (0.03 Cu, 0.44 Fe, 0.32Si) in moving tap water and investigated pitting over a range from one to ten feet per minute. It was found that the number of pits and maximum pit depths both decreased with increasing water velocity until at 8 feet per minute no pitting took place.

Godard et al. (6) report that the movement of a corrosive liquid in contact with aluminum usually accelerates the rate of corrosion, but that this is dependent upon the composition of the electrolyte as well as on turbulence. The role of such movement is probably to prevent the accumulation of acid at the anodic areas and of alkali at the cathodic areas. In addition, movement increases the supply of oxygen to the anode, which enables passivation of local cells.

Godard and Booth (7) investigated pitting caused by natural sea water flowing in aluminum alloy (0.02 Cu, 0.21 Fe, 0.11 Si, 0.016 Ti) pipes at varying velocities. Due to the variability of the flow rate, results were reported in terms of velocity relative to a given pipe diameter. It was found that the rate of pitting decreased up to a certain velocity, then increased as the velocity increased further. Pits at the higher flow rates were narrow and elongated in the direction of flow. As pointed out by the authors,

"Unfortunately, it was not possible to control the water flow rates over the test period and no quantitative conclusions can be drawn". Another problem cited was the possible deposition of copper from some copper-nickel alloy piping upstream of the test specimens. Aziz (8) presents a more detailed extreme value analysis of this data.

As reported by Schwerdtfeger (9), "... the application of cathodic protection to aluminum is fraught with many uncertainties". He investigated 6063-T5 aluminum alloy in a stagnant salt solution (3 percent sodium chloride) over a period of six months. He obtained polarization curves and used these curves to determine the potential required to cathodically protect the specimens. He suggests that the potential corresponding to the beginning of the hydrogen over-voltage curve is a reasonable protection criterion. He reports that a potential of -1.5 V (vs. a saturated calomel electrode (S.C.E.)) caused cathodic corrosion presumably because of the excessive current required to maintain the potential. Cathodic corrosion of amphoteric metals is caused by the generation of excess alkalies at the surface of overprotected metals which leads to increased attack (10). Morgan (11), however, points out that in moving sea water it is difficult to cause cathodic attack.

Shreir (12), Butler and Ison (13), Crennell (14), and Morgan (15), recommend a cathodic protection potential of -0.85V relative to the copper/copper-sulfate half cell for commercially pure aluminum in sea water. Morgan (16) points out, however, that

aluminum alloys used to clad the structural alloys generally display potentials more negative than this in sea water, and that in limited cathodic protection tests a swing potential criterion of -100mV to -200mV has been adopted. Fukutani (17) recommends a protective potential of -0.91V relative to Cu/CuSO_4 for "aluminum alloy", but also recommends that if the protective potential of a metal is not known, protection will be attained by depression of its natural potential by as much as 200mV to 300mV .

Present Work

The overall objective of the work described here was to determine criteria for the protection of aluminum in moving sea water. In order to reproduce actual field conditions, a large specimen was used and natural sea water was pumped directly to the test facility with only sand filtration. The work proceeded in three phases. The first consisted of test facility construction and trial operation. The second phase was that of obtaining polarization curves at speeds from 0 to 3 knots, and from which one could determine cathodic protection potentials. The third phase was a study of the relation between the current density required to maintain the selected potential, and the length of time such cathodic protection was applied. The test facility, methods of data acquisition, and results will be reported in the following sections.

EXPERIMENTAL

This investigation was conducted during June and July at the Rosenstiel School of Marine and Atmospheric Sciences located on Virginia Key. The specimen was moved at velocities from 0 to 3 knots through natural sea water at the end of a rotating beam which was mounted over a 12 foot diameter swimming pool (see Figure 1). Appendix 1 provides a detailed description of the test facility.

Natural sea water was circulated through the pool as shown in Figure 2. The salinity of the sea water in the pool varied from 33⁰/₀₀ to 36⁰/₀₀. During dry periods in June and July, evaporation increases the salinity of Biscayne Bay. Higher salinities are generally encountered in Bear Cut on the ebb tide at this time of the year due to the discharge of the more saline waters of the Bay. The water temperature was 28°C ± 3°C.

Specimen

The alloy chosen for this study was alloy 5086-H34. Table I shows the composition of this alloy. The 5000 series is a non-heat-treatable group of weldable magnesium-manganese alloys. Non-heat-treatable alloys are used where corrosion resistance is

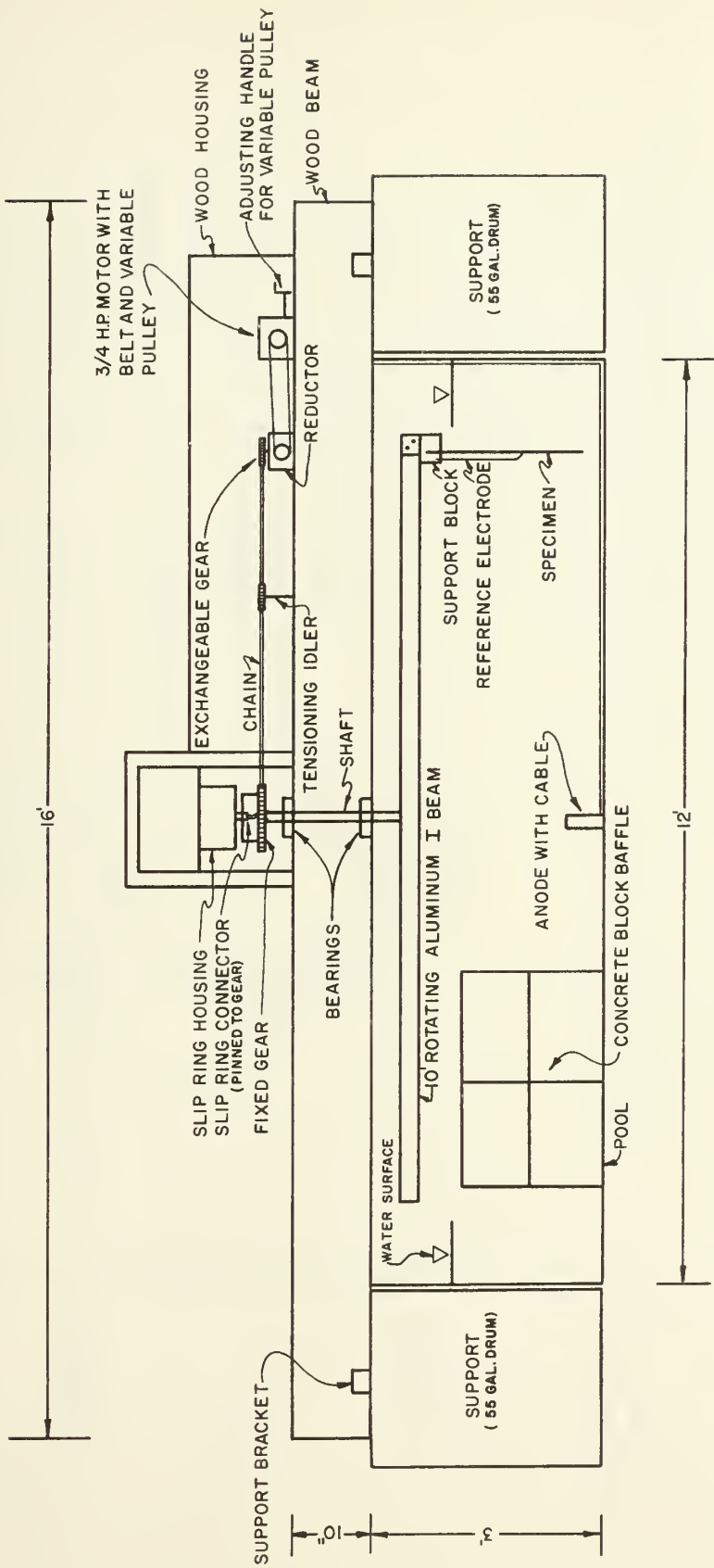


FIGURE 1
TEST FACILITY

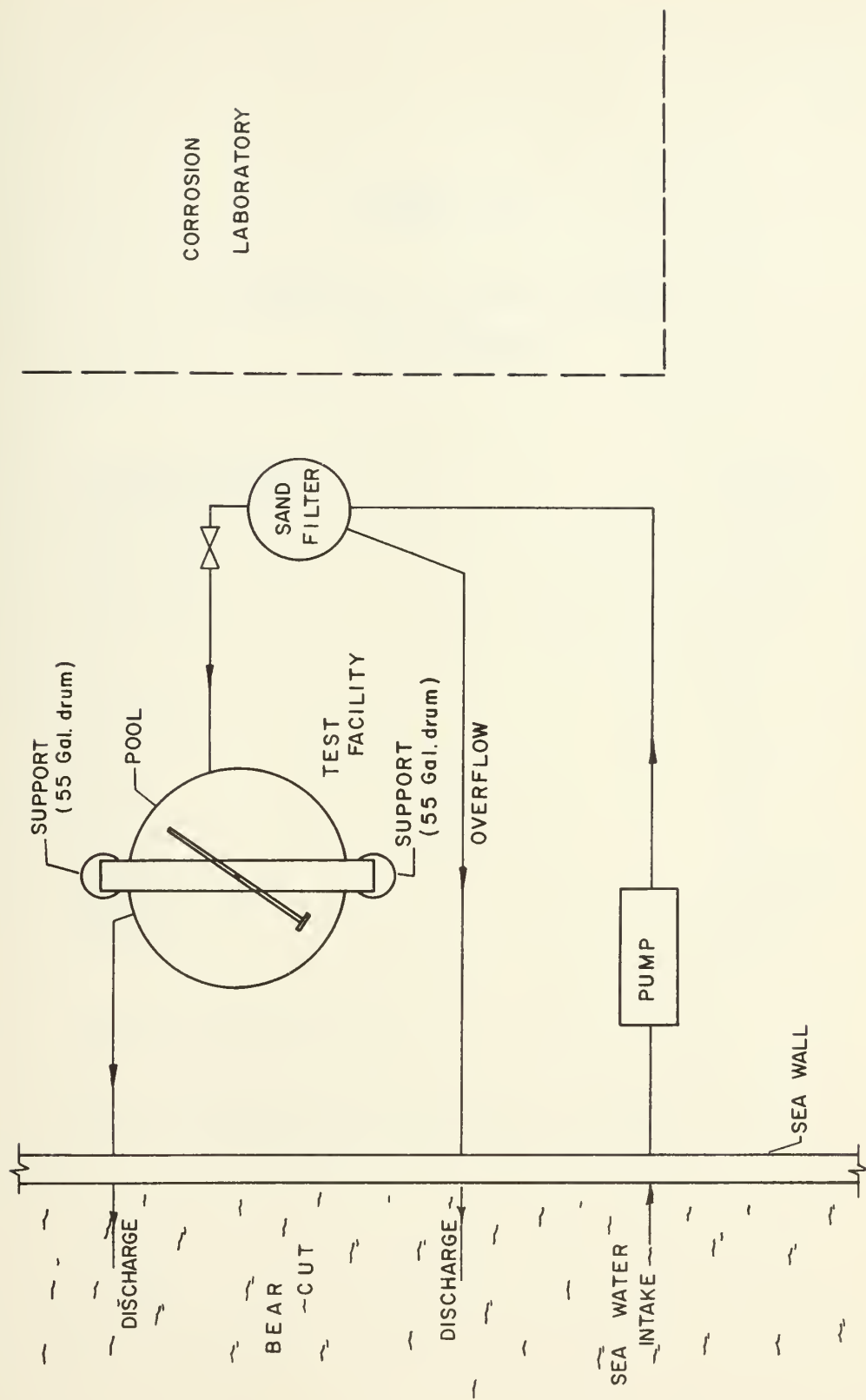


FIGURE 2
SEA WATER CIRCULATION SYSTEM

TABLE I (23)

Composition of Aluminum Specimen

Alloy 5086-H34

<u>Alloying Element</u>	<u>Percent</u>
Magnesium	3.5-4.5
Manganese	0.2-0.7
Iron	0.5
Silicon	0.4
Zinc	0.25
Copper	0.1
Chromium	0.05-0.25
Titanium	0.15

Single values are maxima

Corrosion Laboratory Designation: Al-13-2

important (18), and the 5000 series aluminum-magnesium alloys have been generally adopted around the world for use in marine environments (19, 20, 21). Alloys of the 5000 series have high resistance to corrosion, and economy equal to other non-heat-treatable alloys. They have high weld-zone ductility and superior strength characteristics across the weld zone.

According to Leveau (22), alloy 5086 is a sheet and plate alloy that complements 5083. Alloy 5083 is in use for armor plate and heavy welded structural members for military vehicles and boats, and for ship construction such as deck houses, gun mounts, and stacks. Alloy 5086 is lower in cost than 5083, and somewhat lower in strength; yet it is more readily formed and has good weldability and ductility.

The designation H34 denotes the temper of the alloy. Temper designations indicate the extent of either cold working or heat treatment given an aluminum product during the fabrication process. There are four basic tempers: F-as fabricated, O-annealed, H-strain hardened, and T-heat treated. H, strain hardened, means that the metal has been cold worked to increase its mechanical properties. The 3 designates that it has been strain hardened and stabilized. Stabilizing means low-temperature heating, following strain hardening, which results in increased ductility and stabilized properties, but also in slightly lower strength. The 4 designates the degree of control of temper or mechanical properties within the range designated by H3 (24).

Specimen Mounting

The method used to mount the specimen is shown in Figure 3. The specimen sheet measured 0.063" x 30" x 30". An oak board was cut in the arc of a 10' diameter circle the specimen would travel. The two portions of the board were then bolted together with the top of the specimen between them. This caused the specimen to curve, so as to reduce drag and turbulence. Although the curve of the specimen was not as great near the bottom of the specimen, no problems from turbulence were experienced. Two pieces of angle were used to bolt the oak frame to the aluminum beam.

A $\frac{1}{2}$ " aluminum rod was secured in a hole in the oak frame and passed along the face of the specimen approximately 2" above the surface. This rod was used to support the reference electrode tip, which will be discussed in more detail in following sections. A wood dowel was initially used in this role but prolonged immersion reduced the strength of the dowel to the point where vibration was detected.

The outward surface and the top 6" of the inward surface of the specimen were coated with a coal-tar epoxy. Four parts of Component "A" to one part of Component "B" of Koppers Bitumastic No. 300-M was used for this surface coating. This coating performed very well during the tests and showed no signs of wear. This left an exposed area of 3.80 square feet facing the anode in the center of the pool. It was necessary to cover the top 6" of the specimen because the wake of the specimen as it moved through

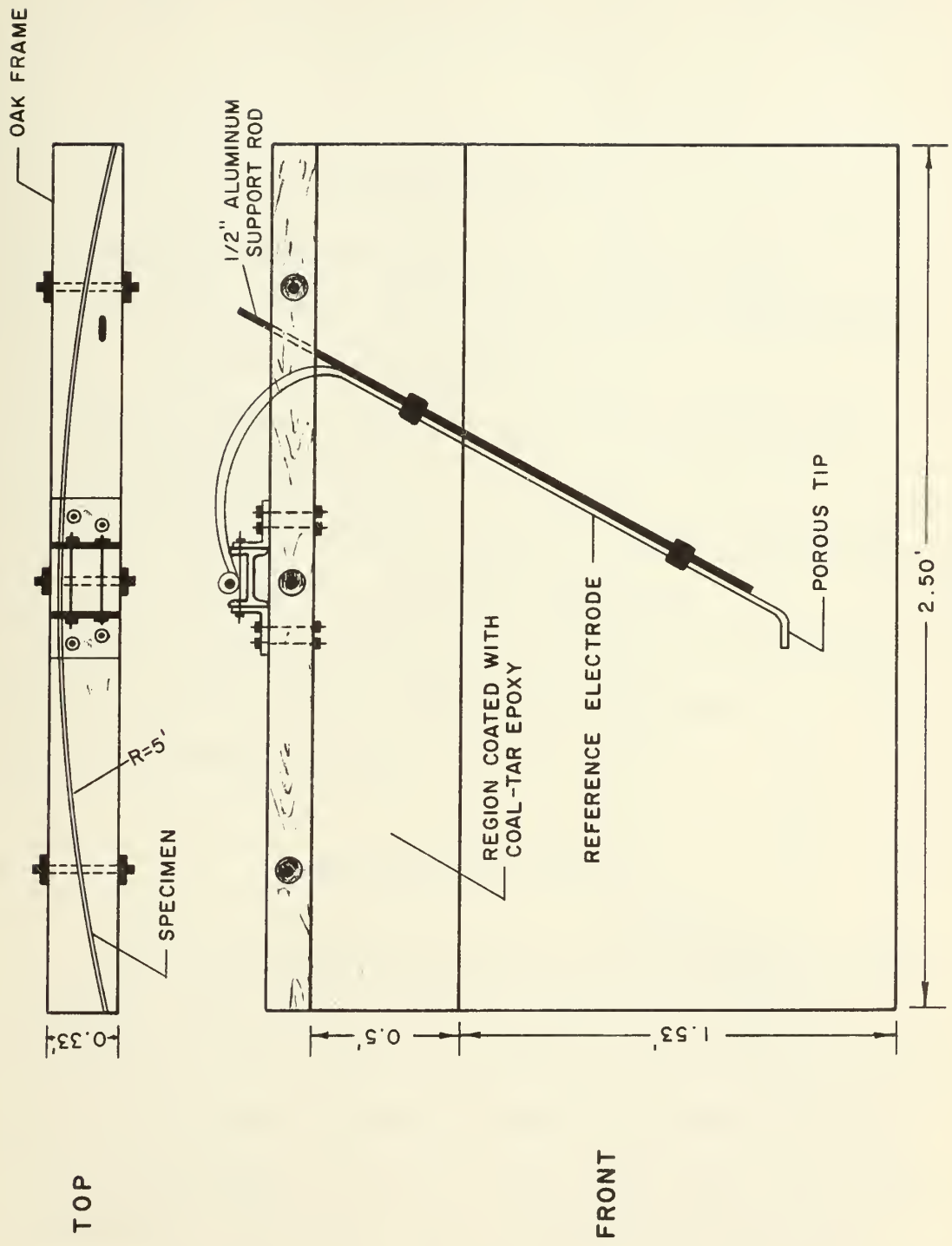


FIGURE 3
SPECIMEN

the water caused a certain splash zone. At velocities up to three knots no portion of the uncoated area was in this splash zone.

Specimen Preparation

The specimen was prepared in the following manner:

- 1) Polish with 280 grit waterproof silicon carbide paper (Wet-or-Dry Tri-M-Ite Paper).
- 2) Rinse with tap water to remove loose corrosion and abrasion products.
- 3) Polish with 400 grit waterproof silicon carbide paper only parallel to the direction of flow.
- 4) Rinse with tap water, insuring that the water drains freely from the surface without "breaking".
- 5) Rinse with acetone.

Reference Electrode

The reference electrode chosen for this study was the copper-saturated copper sulfate electrode. This type of reference electrode was chosen because of its ease of construction, stability, and, as pointed out by Compton, because "the potential criteria for cathodic protection have to a large extent been based on this electrode as a reference" (25). The particular electrode configuration utilized is shown in Figure 4, with a high purity copper rod immersed in a saturated solution of copper sulfate. A detailed description of reference electrodes has been presented by Ives and Janz (26).

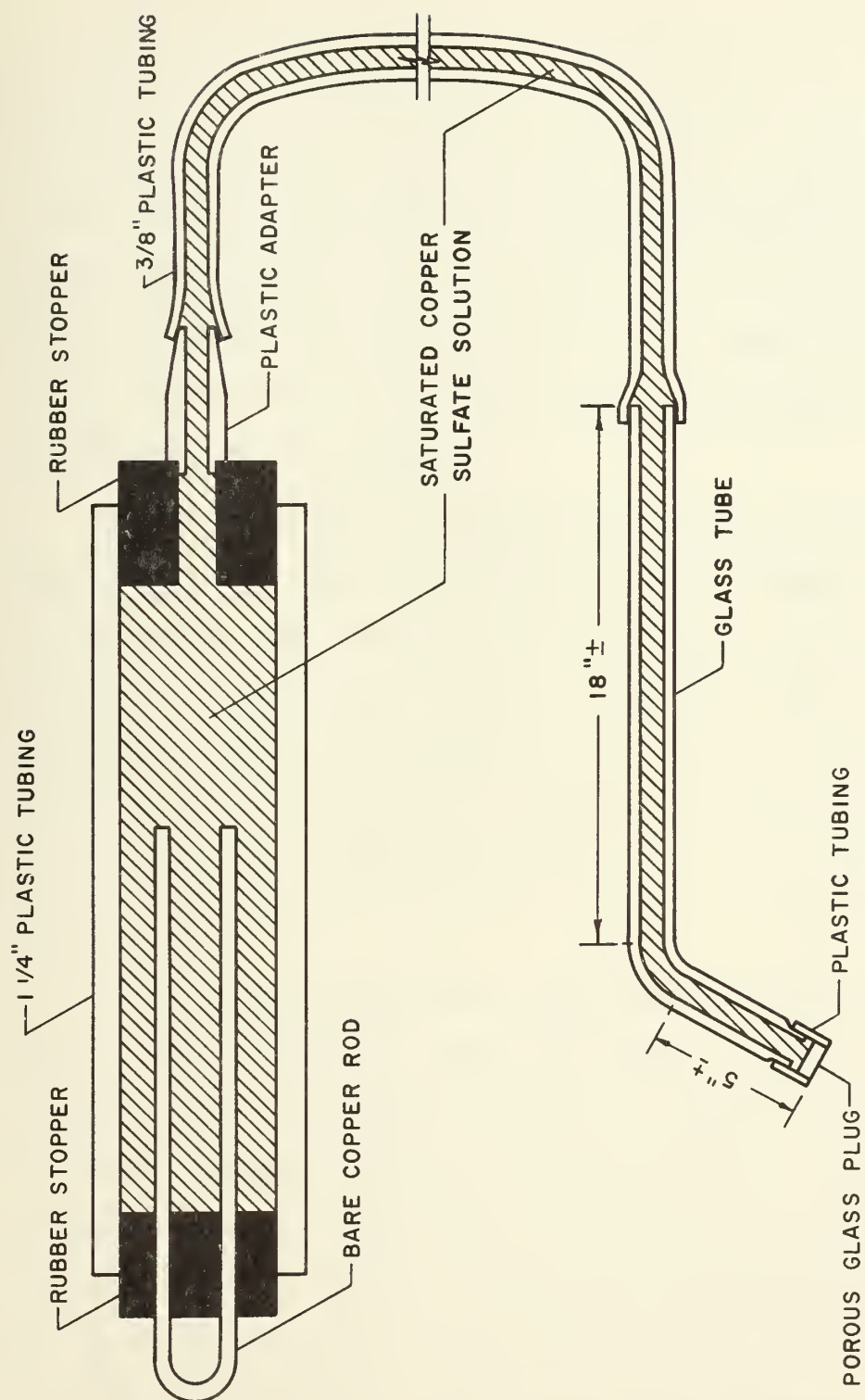


FIGURE 4
REFERENCE ELECTRODE
 NOT TO SCALE

A porous glass plug was used to allow electrolytic contact with the other half of the cell. Corning Porous Glass No. 7930 was used for the plug. There is some error due to electrocapilarity within this plug, and due to concentration potentials between liquids (27), but this plug was found to be the best available method of providing a junction. An attempt was made to use an asbestos fiber to provide electrolytic contact but it proved unreliable at velocity.

As shown in Figure 3, the glass tube (10mm) was fastened to the aluminum rod. This was accomplished by using segments of plastic tubing and a clamp to hold the porous tip against the specimen. The short piece of plastic tubing which held the porous tip in place on the glass tube also acted as a shock absorber in case of vibration. The segment of $1\frac{1}{4}$ " tubing which contained the copper rod was placed on the web of the rotating aluminum beam.

A Corning Calomel (mercurous chloride) Reference Electrode Number 476002 was used as a check on the copper-saturated copper sulfate electrode. As shown in Table II, the American Society for Testing and Materials gives a potential difference between the copper-saturated copper sulfate electrode and the saturated calomel electrode of +0.06 V. The potential difference between the two electrodes in use in this study was found to be +0.065 V. The Cu/CuSO_4 electrode was checked against the SCE after each test run and if it was found to vary more than 1 mV from 0.065 V then the copper rod was scraped and new saturated copper sulfate

TABLE II (29)

Reference Electrode Conversion Factors

To convert from one scale to another, add the values indicated below:

<u>From (E')</u>	<u>To SHE Scale</u>	<u>To SCE Scale (E')</u>
H_2/H^+		-0.241 V
Ag/AgCl 1 M KCl	+0.235 V	-0.006
Ag/AgCl sat KCl	+0.200	-0.041
Hg/Hg ₂ Cl ₂ , sat.	+0.241	
Hg/Hg ₂ Cl ₂ , 1 M	+0.280	+0.039
Hg/Hg ₂ Cl ₂ 0.1 M	+0.334	+0.093
Cu/CuSO ₄ , sat.	+0.30	+0.06

solution added. It was found that even after extended runs of six days the variation was no more than 2 mV. This is considered acceptable when compared with data published by Compton (28). He reports that a study of 120 different copper sulfate electrodes measured against one as a standard with moist soil as the salt bridge resulted in a standard deviation of 2.7 mV.

Polarization Measurements

In this investigation the polarization technique was used for detection and measurement of corrosion. According to Uhlig (30), "The extent of potential change caused by net current to or from an electrode, measured in volts, is called polarization". Stern (31, 32) has developed the polarization technique into an excellent tool for corrosion testing. The polarization technique was chosen over the traditional method of measuring weight loss per unit area over a given time interval because the latter is both time consuming and leads to results which are often not repeatable. Further, in sea water any attack which does develop is likely to be extremely localized (pitting), and thus weight change data is of little value (33).

The galvanostatic polarization technique was used to obtain the cathodic polarization curves. Figure 5 depicts the circuit utilized. UF cable was used to connect the test facility and the instruments located inside the Corrosion Laboratory. A mercury cell placed on the end of the rotating beam was used to check the circuit. It was found that the 50 foot leads had virtually no

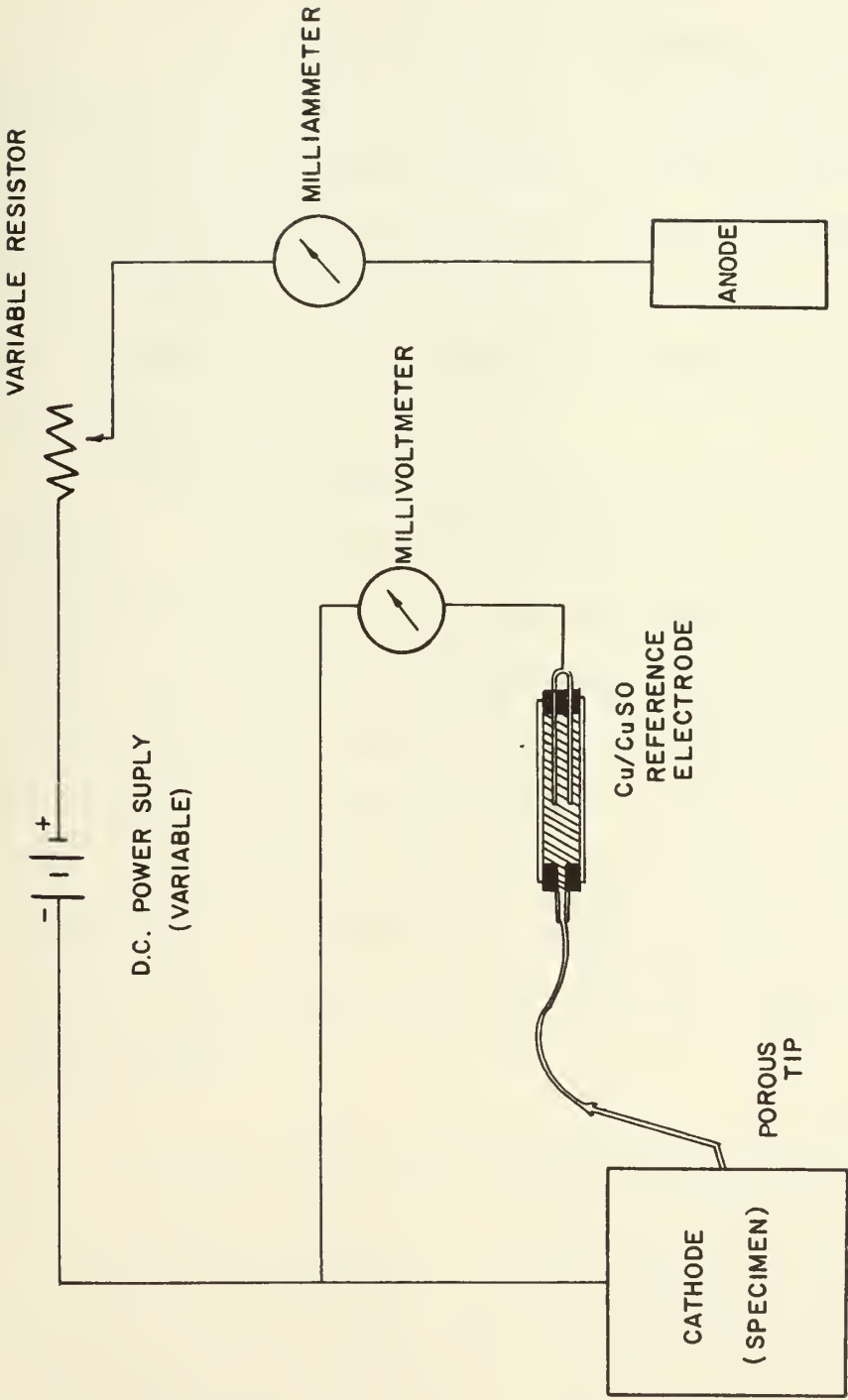


FIGURE 5
POLARIZATION CIRCUIT
SCHEMATIC DIAGRAM

effect, with losses much less than 1 mV. A Harrison Laboratories 0-18 volt Direct Current Power Supply No1 6263A was used as a power source. A variable resistor was used in series to provide exact adjustment at very low current levels. A Weston No. 1240 (Serial 232) digital potentiometric voltmeter was used to measure potential, and a Sensitive Research Milliammeter (Serial U24784) was used to measure current. A Duriron* anode was placed in the center of the pool (see Figure 1). This anode had a specific resistance of 72 microhm-centimeters at 20°C.

The following procedure was followed in making polarization test runs. A period of one hour was allowed to obtain a stable open circuit potential. After this time period, current was applied and increased in increments until the desired polarization curve was obtained. This was done in the low current range with the variable resistor as mentioned above, and in the higher current ranges with the voltage adjustment on the power supply. It was found that 3 minutes was a sufficient time for conditions to stabilize, and that interval was used on all runs for each current interval.

Cathodic Protection System and Measurements

Cathodic protection by the application of an external current has proven to be a feasible means of preventing the corrosion of metal structures when they are in contact with an electrolyte (34).

*Duriron is a trade name for a high silicon iron alloy used for anodes.

This external current polarizes the protected metal to a point where all of the local anodes on the surface become cathodes, thus stopping the corrosion. Figure 6 shows the circuit used to apply external current to the specimen. The key to this system is the Brinkman Wenking Potentiostat Model 68TS (Serial 7859).

A potentiostat is essentially a controller that measures a voltage in an electrochemical cell, compares it with a set voltage constant, and alters the cell current until the controlled voltage (the measured variable) equals the voltage setting (desired value). Reactions which take place in the cell do not affect the functioning of the regulatory system. The desired voltage was obtained from an internal voltage generator consisting of a long-life battery and a 10-turn precision potentiometer. This instrument maintained the desired cathodic protection potential within 2 mV, which is considered excellent when it is noted that the instrument is not recommended for use with input leads longer than a few feet.

An Esterline-Angus Graphic Ammeter was used to record current versus time, and the same Duriron anode mentioned previously was used. Periodic checks of the system were made to insure proper operation. After the runs, the specimen was removed for examination of its surface condition.

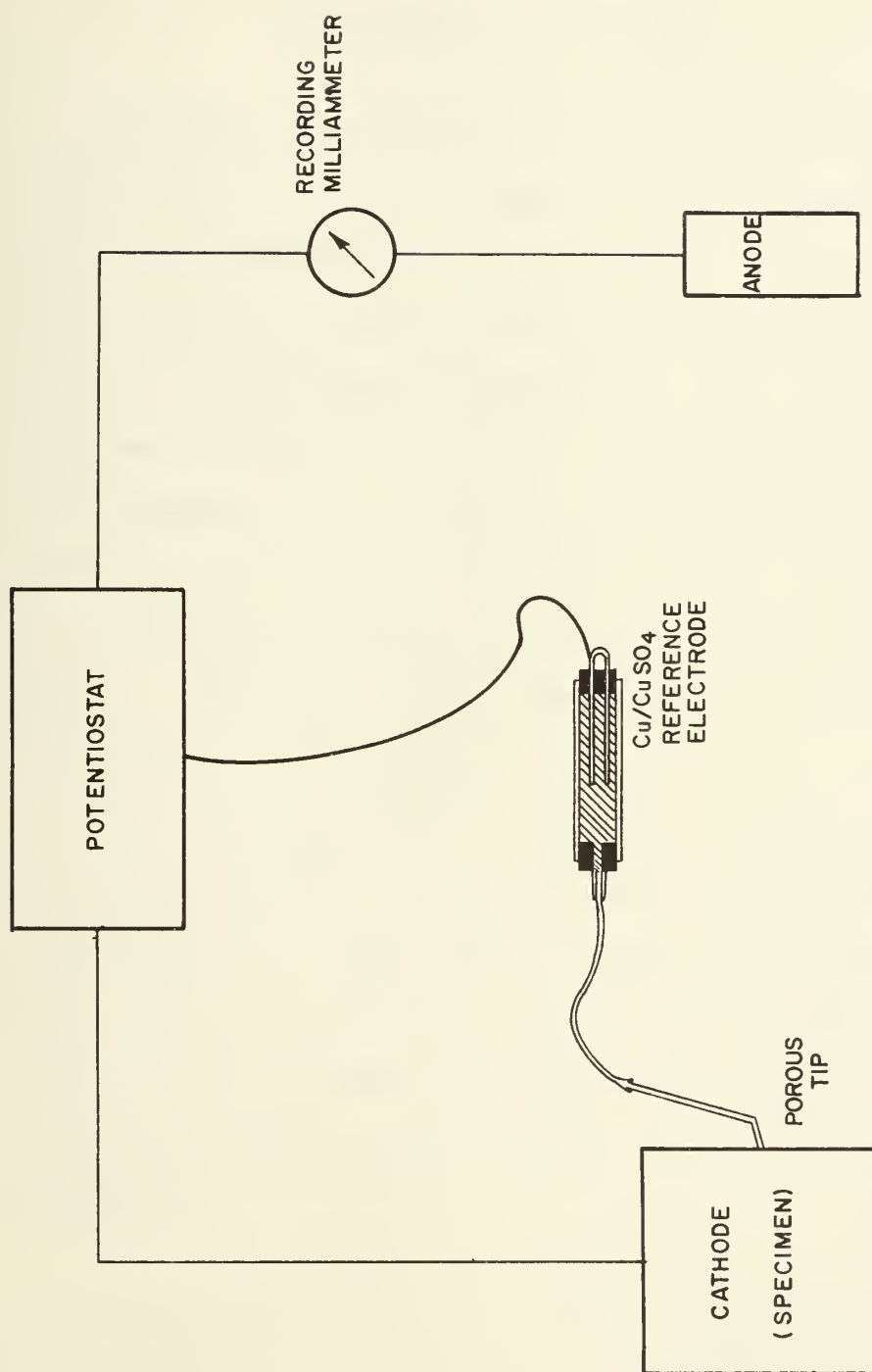


FIGURE 6
CATHODIC PROTECTION CIRCUIT
SCHEMATIC DIAGRAM

RESULTS

Cathodic Polarization Curves

A minimum of three cathodic polarization curves each were run on the specimen for velocities of 1, 2, and 3 knots, as well as at rest. The curves were run in a random sequence over a two week period to guard against repeating any possible error through the entire investigation of one velocity. These curves are presented in Figures 7 through 10. These curves were found to be quite repeatable, and for this reason different symbols were used to help identify the three runs at each velocity. An average curve for each velocity was calculated and these are plotted in Figure 11. The symbols used in Figure 11 are not related to those used in previous figures.

Also plotted on Figures 7 through 10 are lines representing the respective slopes of the Tafel regions where the polarizing overvoltage varies linearly with the log of the polarizing current (the straight-line portion of the curve after it bends down). The slope of the polarization curve in the Tafel region (β), can be calculated using the Tafel equation (35). This equation is shown below:

$$\eta = \beta \log \frac{i}{i_0}$$

where η = overvoltage in volts

β = slope of curve in Tafel region

i = current in amps at any η

i_0 = exchange current

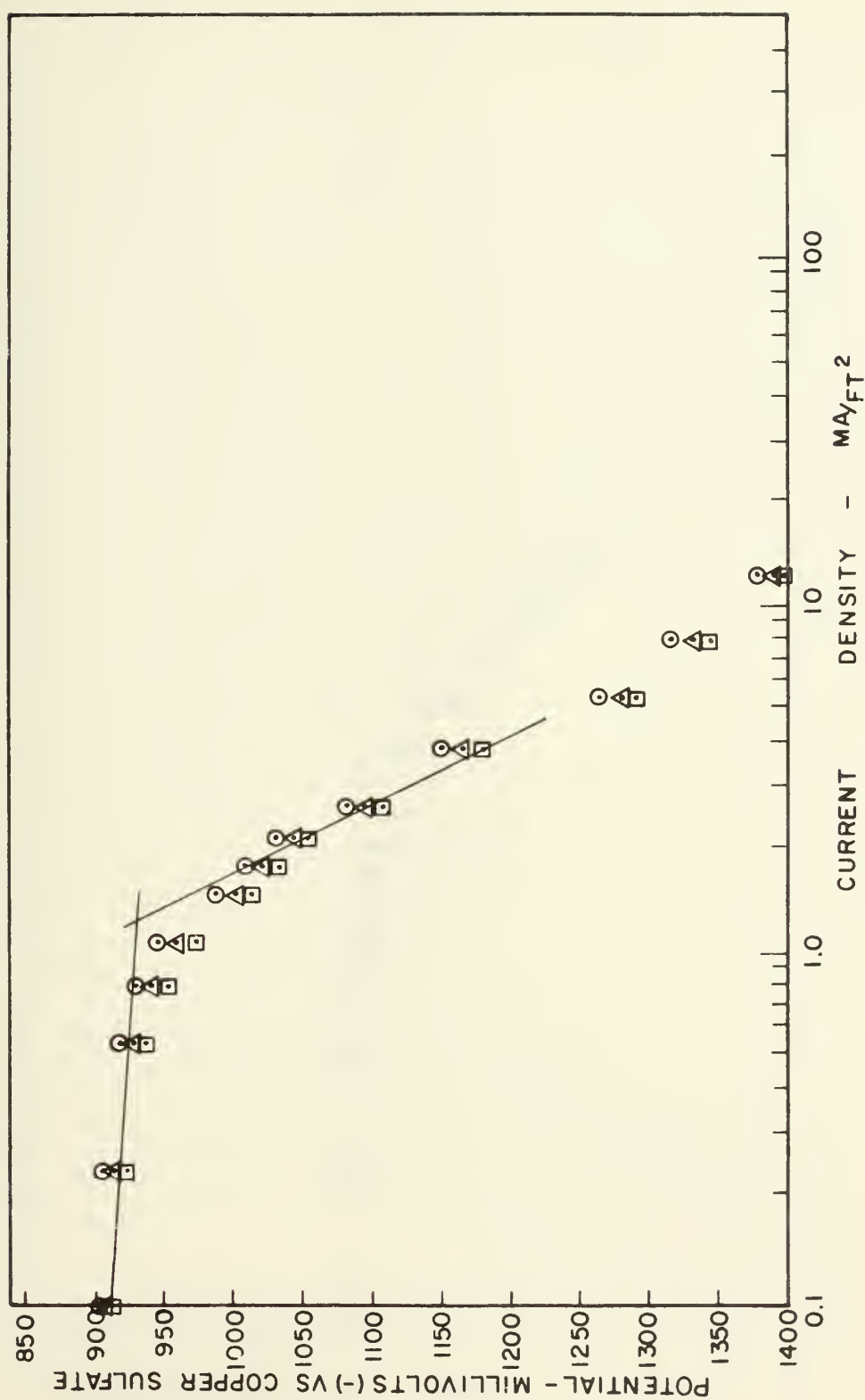


FIGURE 7
CATHODIC POLARIZATION CURVES
STATIONARY

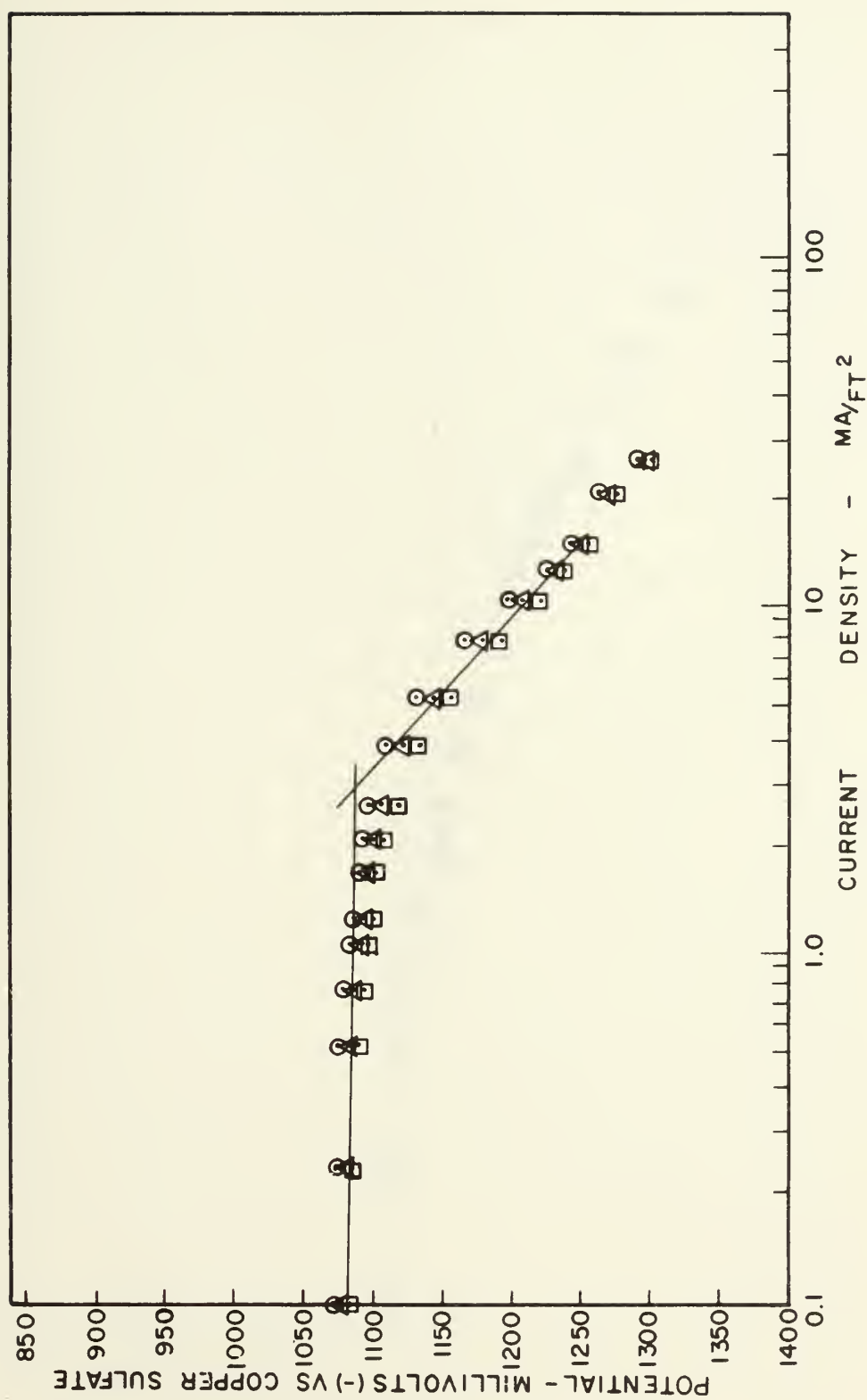


FIGURE 8
CATHODIC POLARIZATION CURVES
ONE KNOT (1.69 FT/SEC)

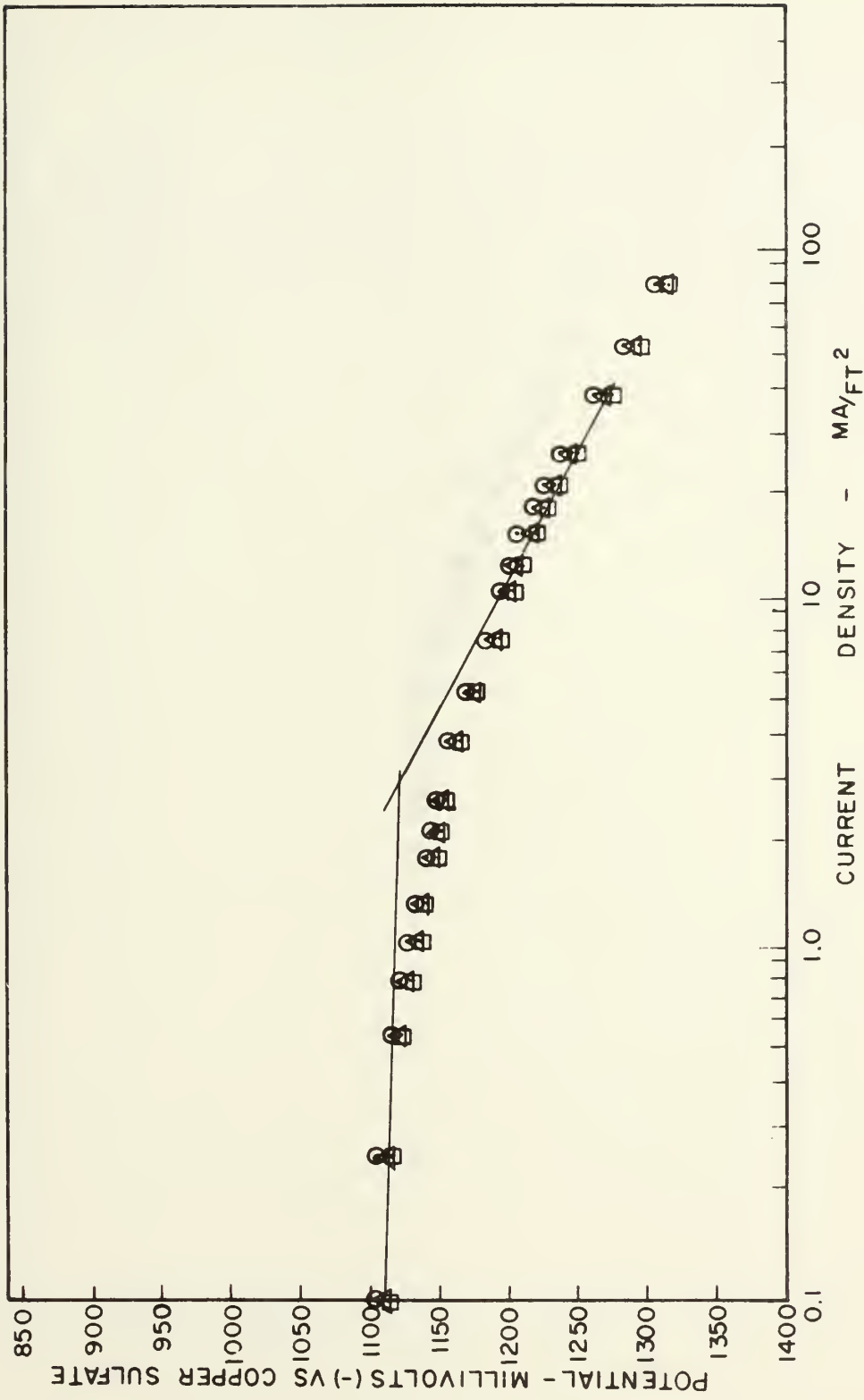


FIGURE 9
CATHODIC POLARIZATION CURVES
TWO KNOTS
(3.38 FT/SEC)

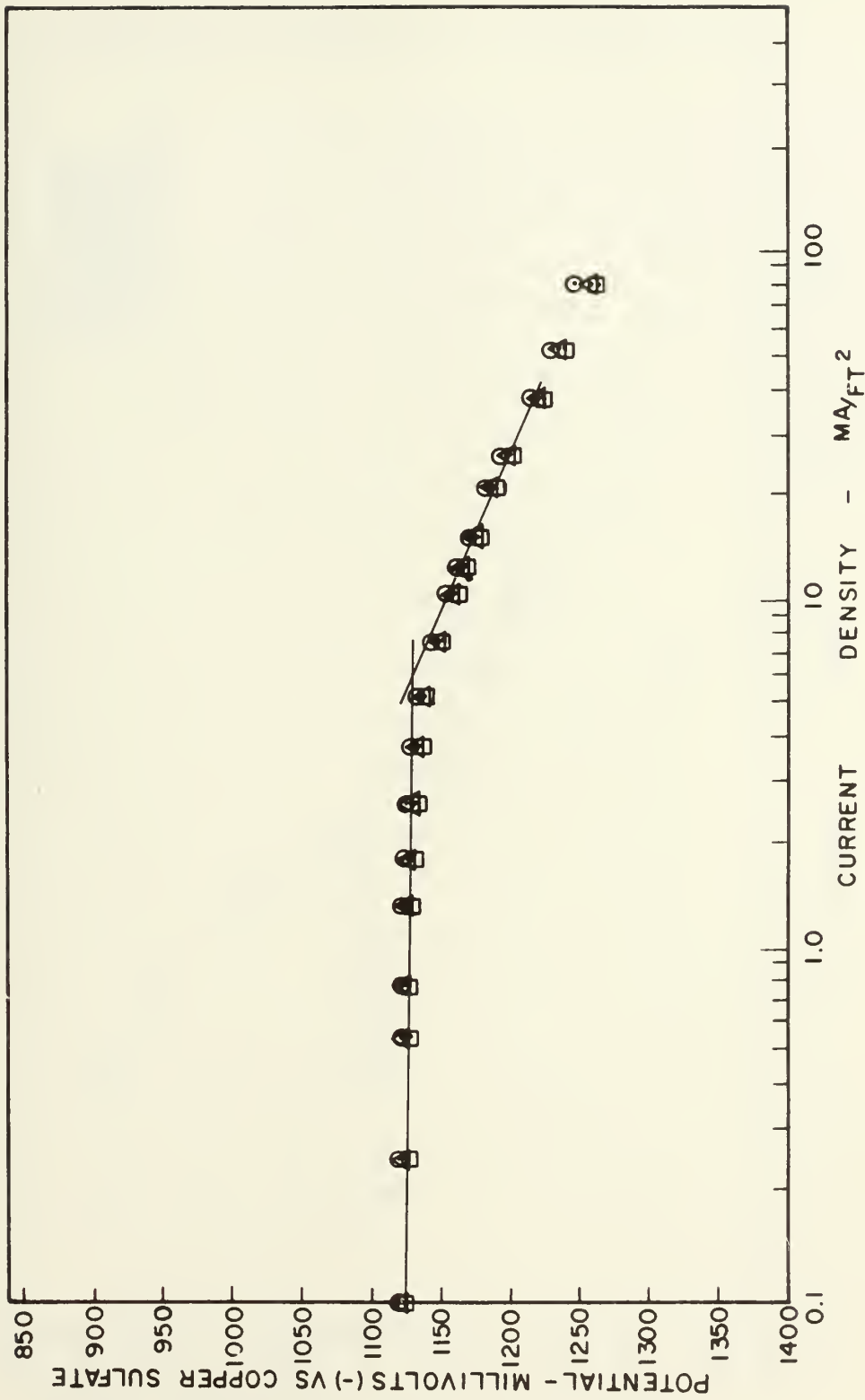


FIGURE 10
CATHODIC POLARIZATION CURVES
THREE KNOTS (5.06 FT/SEC)

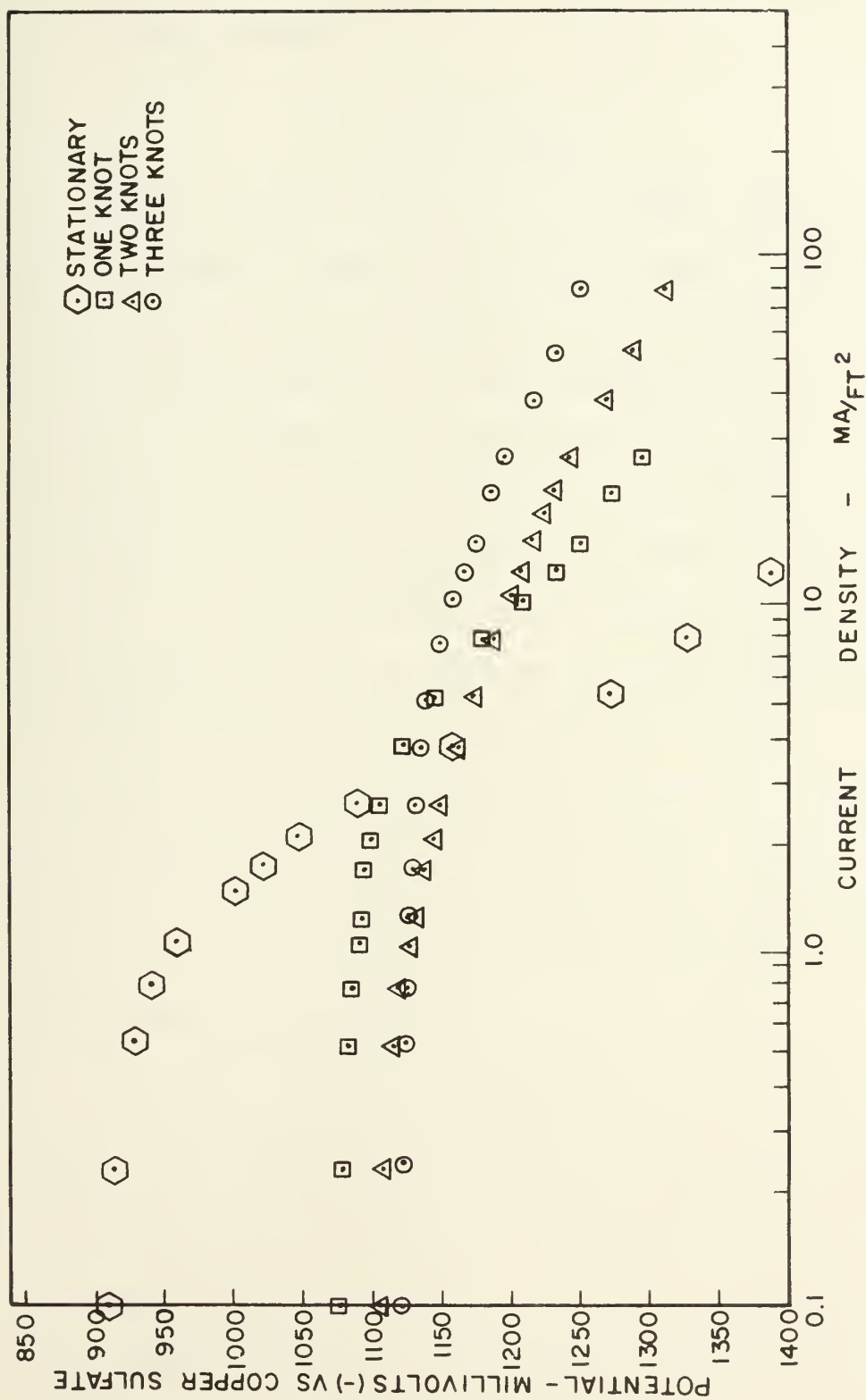


FIGURE 11
CATHODIC POLARIZATION CURVES
SUMMARY

If two points on the polarization curve are known, β can be determined as follows:

$$\beta = \frac{\eta_1 - \eta_2}{\log i_1 - \log i_2}$$

There are several trends which are apparent. First, the open circuit potential becomes more negative as velocity is increased. The average open circuit potential values are shown in Table III. The open circuit potential of the stationary specimen (-0.909 V) compares very favorably with that reported by Dix et al. (36). They report an open circuit potential for alloy 5086 in synthetic sea water (53g NaCl + 3g H₂O₂ per liter at 25°C) of -0.850 V against a saturated calomel electrode. Using the conversion chart shown in Table II, this is equivalent to -0.910 V against the Cu/CuSO₄ reference electrode. It should be noted that it was necessary to disconnect the Harrison Laboratories power supply while obtaining the open circuit potential, even though it was turned off. This was necessary because the power supply produced a small d.c. voltage of reversed polarity which tended to drive the specimen slightly anodic.

The second trend noted was that as velocity increased, there was an increase in the current density required to maintain the theoretical point of cathodic protection. This point is the intersection of the extended initial straight-line portion of the polarization curve and the Tafel slope. These values are presented in Table III. However, the corrosion reaction under consideration is not that of a simple cell. The surface consists of a

TABLE III

Polarization Curve Data

	<u>Velocity (Knots)</u>			
	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>
Open Circuit Potential (Volts vs Cu/CuSO ₄)	-0.909	-1.080	-1.116	-1.122
Corrosion Current Density (ma/ft ²) Required for Theoretical Protection Criteria (knee)	1.02	2.85	2.95	5.90
Corrosion Current Density (ma/ft ²) Required for 100 mV Shift Protection Criteria	1.78	7.50	14.50	43.50
Cathodic Beta	0.418	0.224	0.134	0.106

multitude of anodes and cathodes each joined electrically through the metal. Thus, in practice it has been found that the theoretical point of cathodic protection is not a sufficient criterion (37).

In practice two techniques for establishing protection criteria have evolved: 1) a metal will be adequately protected by maintaining the potential of the metal more negative than a certain potential value, and 2) a metal is sufficiently depressed in potential to achieve protection when its potential is altered by a particular amount. According to Morgan (38), criteria established for the more common metals by either or both techniques have been found sufficient and are generally accepted. He further points out that many metals have not been cathodically protected so widely, nor have they been protected in a variety of electrolytes, and that protection criteria for these metals are generally lacking.

With respect to aluminum alloys, Morgan (39) states that a limited range of these alloys have been adequately protected by a 100 mV shift in potential, but that the level of the on-set of cathodic corrosion in different solutions has not been determined. This 100 mV shift from open circuit potential cathodic protection criterion was chosen for use in this investigation. It is felt that such a criterion is as reasonable and certainly more definitive than that proposed by Schwerdtfeger in which the protection criterion is "... the potential corresponding to the beginning of the hydrogen over-voltage curve" (40).

Using the 100 mV shift criterion, current density requirements can be approximated from the polarization curves (see Table III). As with the theoretical protection point (knee)

criteria, there is an increase in current density required as velocity increases. This relationship is also illustrated in Figure 12. The cathodic betas, the calculation of which was described earlier, offer still another tool with which to study this relationship. The respective betas are shown in Table III, indicating the decrease in Tafel slope with increasing velocity.

Current Density vs. Time

This final phase of the investigation was an attempt both to test the 100 mV protection criterion proposed earlier, and to examine the relation between current density and time of protection. Two runs of 5 days each were made, and current density versus time plots of the runs are presented in Figure 13.

The initial run was made at a velocity of 3 knots. The specimen was allowed to stabilize for one hour, at which time the open circuit potential was -1.120 V vs the Cu/CuSO₄ reference electrode. Consequently, a control potential of -1.220 V vs Cu/CuSO₄ was established on the potentiometer. The specimen was stopped for a few minutes and examined after 20 and 97 hours. At both checks no evidence of corrosion was found and current density decreased, only to rise to previous levels within an hour. At the 20 hour check, current density fell from 110.5 ma/ft² to 47.4 ma/ft² or a change of 57.2%. At the 97 hour check it fell from 72.5 ma/ft² to 39.5 ma/ft², or a change of 45.6%. This would tend to indicate that the metal becomes less sensitive to changes in velocity as time of protection increases. It should be noted,

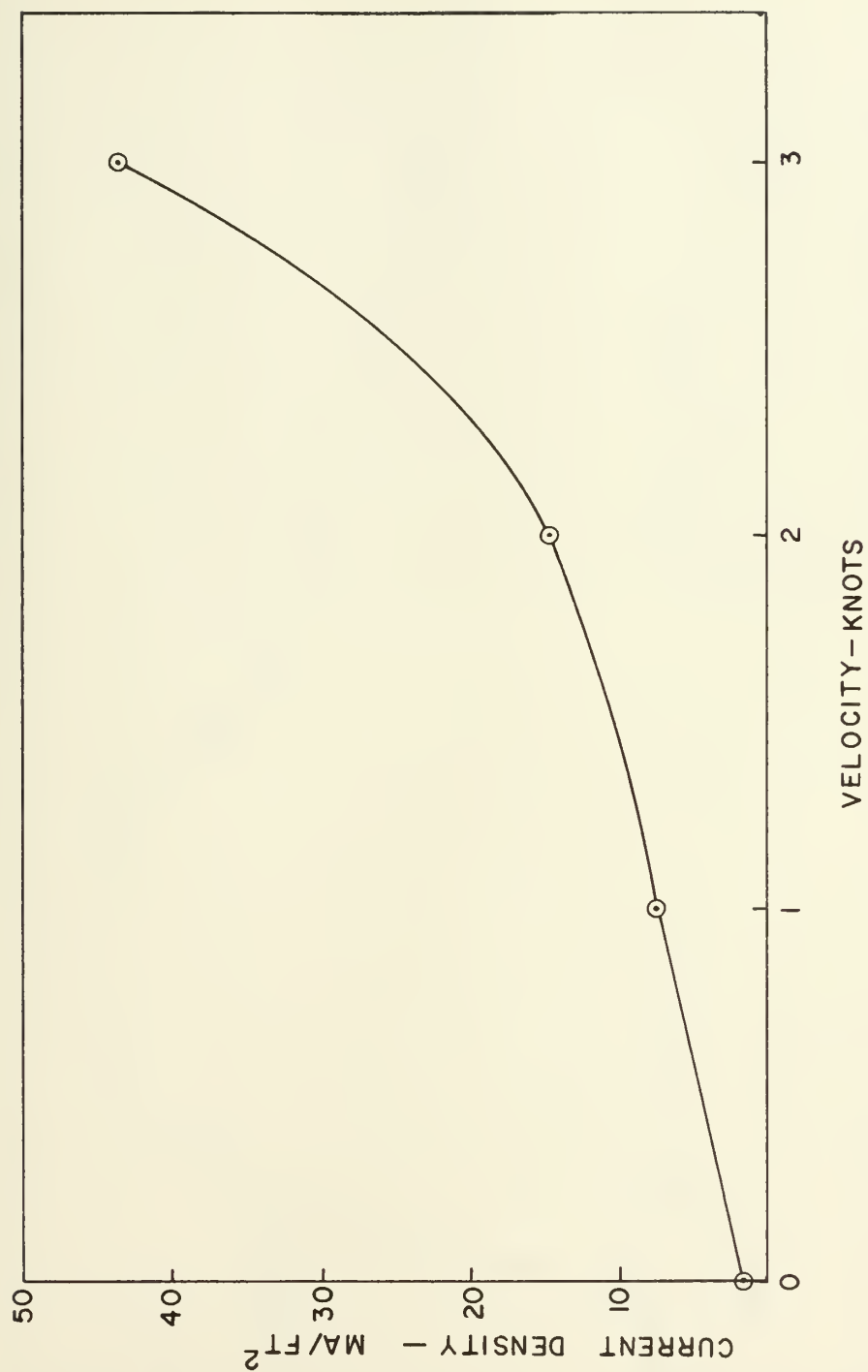


FIGURE 12
CURRENT DENSITY vs. VELOCITY
(100 MV SHIFT CRITERION)

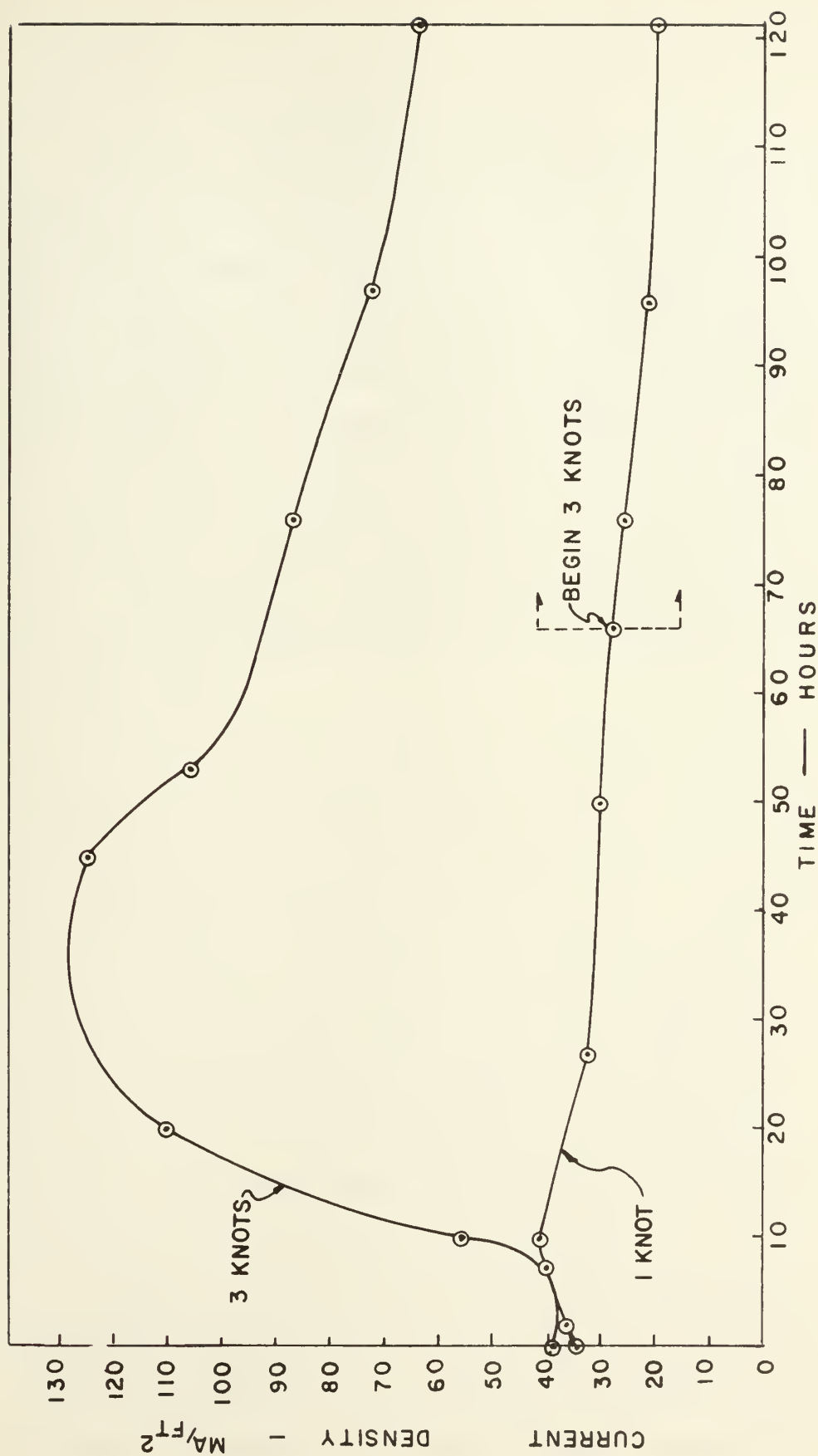


FIGURE 13
CURRENT DENSITY vs. TIME

however, that erosion and other mechanical effects were not encountered at the velocities under investigation.

The 3 knot current density versus time plot indicates that there is an initial rise in current density to a maximum (126.2 ma/ft^2) which is approximately 3 times the level indicated by the 100 mV shift criterion (43.5 ma/ft^2). This is followed by a gradual decrease in current density to a level of about one-half the maximum (63.2 ma/ft^2). This gradual decrease in current density with time is similar to that reported by Copson (41) for other metals, which he reports is due in part to a gradual thickening of protective films. Upon removal of the specimen after 120 hours, examination of the surface revealed an oxide layer but no evidence of pitting or local attack.

Prior to initiation of the 1 knot test, the specimen was prepared in the usual manner. However, after an hour the open circuit potential was -1.210 V vs Cu/CuSO_4 rather than the value of -1.080 obtained during the polarization tests. The specimen remained polarized. The specimen was allowed to stand in the laboratory for 24 hours, at which time it was prepared once again. After one hour the open circuit potential remained -1.210 V . Due to lack of time, and as a further test of the 100 mV shift criterion, the current density versus time test was run with a potential of -1.310 as a protection criteria.

As shown in Figure 13, this 1 knot curve demonstrates the same general characteristics as the 3 knot curve. Once again there was an initial rise to a maximum (42.2 ma/ft^2), however, to a level of approximately 6 times the level indicated by the

100 mV shift criterion (7.5 ma/ft^2). Also, the maximum occurred much earlier in the 1 knot run (10 hours) than in the 3 knot run (35 hours). There is the same gradual decay following the maximum. At 60 hours the current density indicated by the 1 knot plot was 70% of the maximum for that run, while at the 60 hour point of the 3 knot run the current density indicated was 75% of the maximum.

At the 66 hour point it was decided to examine the effect of increasing the velocity, and velocity was increased to 3 knots. This change in velocity had virtually no effect. This may result from the thickening of the oxide layer to a point where changes in velocity at the metal surface do not occur, as suggested by Copson (42) and Romeo et al (43). At the end of the second (combination 1 and 3 knot) run current density had fallen to 19.7 ma/ft^2 , or about one half of the maximum level (42.2) the same as it had in the initial run.

It is believed that the 100 mV shift criterion provided adequate protection for the specimen within the velocities tested. That some protection is necessary was made evident during an unsuccessful cathodic protection run. Owing to an equipment failure, the test was allowed to run, after only a few hours of protection, with an unprotected specimen, at a velocity of 3 knots for approximately 14 hours. Numerous pits were found that were narrow and elongated in the direction of flow.

CONCLUSIONS

The primary objective of this research was to determine criteria for the protection of aluminum alloy 5086 in moving sea water. It is not to be inferred that this research provides sufficient data for the establishment of firm criteria. It does, however, offer data which will aid future investigations and which will throw light on the polarization behavior of aluminum. As the data indicate, increasing the velocity of sea water past 5086 aluminum alloy affects its polarization characteristics in two ways. The open circuit potential becomes more negative, and the current density required to maintain a given potential, increases.

A shift of -100 mV from the open circuit potential appeared to be an adequate criterion for the cathodic protection of this alloy. In both tests in which protection was based on this criterion, there was an initial increase in current density required, followed by a gradual decrease. The rates of decrease with respect to maxima appear to be approximately equal, with one half of the maximum current density being required after 120 hours.

The following recommendations are offered for further study with this particular test facility. (1) If a potentiostat is available, as the Wenking was for the latter portion of this study, it should be used for potentiostatic polarization curves. It was often difficult to hold current constant with the manual galvano-

static technique employed in this investigation. (2) Because of the excessive drag of the reference electrode configuration used, it was not possible to use the larger velocity capabilities of the test facility. It is recommended that a configuration more compatible with higher velocities be adopted.

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APPENDIX 1

TEST FACILITY

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Test Facility

In this facility the specimen was moved at selected velocities through natural sea water at the end of a rotating aluminum beam mounted over a 12 foot diameter swimming pool (see Figure 1). A standard Sears, Roebuck and Company 36" high pool, with sheet steel sides and a vinyl lining was erected on a bed of sand. Two standard 55 gallon barrels with welded steel brackets served as supports for a 16 foot wooden beam constructed of 2" x 10" planks and placed across the pool.

The drive system for the aluminum beam consisted of a 3/4 horsepower constant speed electric motor mounted on an adjustable base. An adjustable pulley and belt connected the motor with a gear reducer. A gear mounted on top of the reductor was connected to a gear mounted on top of the central shaft by a chain, with an adjustable idler mounted between the two gears to remove slack in the chain. Speed adjustment was made possible by a screw adjustment for the motor location which, in turn, varied the speed of the belt. For major speed changes, the gear mounted on top of the reductor could be changed. This necessitated the addition or deletion of a length of drive chain. At regular intervals, the adjustable pulley was greased through an axially mounted fitting, and the drive chain and gear reductor were lubricated with SR-1.

The central shaft was machined from steel rod stock, and was supported by two bearings. A plate was welded to the bottom of the shaft, and the 2" aluminum I-beam was bolted through the web to this plate, with a bearing plate being used to distribute the stress in the web. The shaft was drilled from the bottom up the center past the first bearing, and then slotted for the remainder of its length. This allowed wires to be brought from the specimen mounted at the end of the beam to the base of the shaft and then up the shaft through the bearings.

A five conductor silver contact slip ring assembly was used at the top of the shaft. The assembly was previously used in connection with acoustical studies, and was of such a quality that it offered no discernible noise to readings made during this investigation. The slip ring assembly was mounted above the shaft in such a manner that the rotating core was directed down in line with the main shaft. A metal yoke was attached to the rotating core of the slip ring, and the yoke in turn had two 1/2" diameter rods which were aligned with two holes in the gear which topped the shaft. Thus, as the gear turned, so did the rotating core. The slip ring housing was mounted upon a wooden frame. The gear and central shaft were connected by a shear pin, which was dropped vertically through properly aligned holes in the gear and shaft. A large diameter nail was found to be a suitable shear pin.

It was found that it was possible to start the motor at speeds up to 3 knots without damage, but during tests the motor was always

started at the minimum speed position (approximately $3/4$ knot), and subsequently adjusted to the required speed. Specimen velocity was determined with a stop watch, knowing the circle it traveled to be 31.41 feet. Several concrete block baffles were required to retard water movement, a method which proved quite effective in the range of speeds investigated. Once the proper motor adjustment was determined for a particular speed, this position was marked on the base and adjusting handle to facilitate repetition of velocity.

The entire chain drive and slip ring assembly system was enclosed by a wood housing to protect it from wind and rain. The bottom of the beam was left open to provide for adequate ventilation to prevent condensation. There was no evidence of overheating of the motor. Protective screens were constructed over the pool to keep out debris. Electrical connections (110 V) were encased in a water resistant junction box, which also provided an outlet for power tools and test instruments. A buried cable provided this power from the Corrosion Laboratory.

Natural sea water is being pumped continuously from Bear Cut to large settling tanks on the roof of a nearby building. These tanks tended to damp salinity fluctuations. From the settling tanks, the water is distributed to individual laboratories, including the Corrosion Laboratory. With the exception of a stainless steel pump casing and impellor, the sea water traveled through polyvinyl chloride pipes and fittings. The water was then passed through a gravity feed sand filter, which measured approximately 10 feet high and 4 feet in diameter. This filter acted not

only as a reservoir, but also removed most of the suspended silt in the sea water. The level of sea water in the pool was controlled by an adjustable overflow pipe, which also acted as a skimmer.

VITA

LT. Richard Hardwicke Rice, Jr., CEC, USN, was born in Corpus Christi, Texas, on April 17, 1945. His parents were Richard Hardwicke Rice and Dora Deane Rice. He received his elementary education at several California, Florida, Rhode Island, and Virginia schools, and his secondary education at Monterey High School in Monterey, California. In July, 1963 he entered the United States Military Academy from which he was graduated with the B. S. degree in June, 1967. He was commissioned an Ensign in the Civil Engineer Corps of the United States Navy and from June 1967 until August 1968, he served with U. S. Naval Mobile Construction Battalion FIVE in Vietnam. In September 1968, he entered Stanford University from which he was graduated with the M. S. (Civil Engineering) degree in August 1969.

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of aluminum alloy 5086
in sea water.

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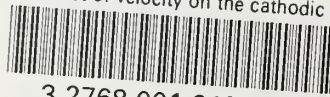
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